# Why dry etching?

Dry etching advantages

- Eliminates handling of dangerous acids and solvents
- Uses small amounts of chemicals (gas)
- Isotropic or anisotropic/vertical etch profiles
- Directional etching without using the crystal orientation of Si
- High resolution and cleanliness
- Less undercutting
- Better process control -> reproducibility (??)

Dry etching disadvantages:

- Some gases are quite toxic and corrosive.
- Re-deposition of non-volatile compound on wafers.
- Expensive equipment ($200-500K for R&D, few million for industrial tools ).

# Types of dry etching

Non-plasma based - uses spontaneous reaction of appropriate reactive gas mixture.

Plasma based - uses radio frequency (RF) power to drive chemical reaction.

## Xenon di-fluoride ($XeF_2$) etching of Si:

$$2XeF_2 + Si \rightarrow 2Xe\ (g) + SiF_4\ (g)$$

- $XeF_2$ is a white powder, with vapor pressure ~3.8 Torr at 25$^{o}$C.
- Isotropic etching, non-polish etching (rough)
- High selectivity for Al, $SiO_2$, $Si_3N_4$, photoresist.
- Typical etch rate ~1µm/min
- Heat is generated during exothermic reaction
- $XeF_2$ reacts with water (or vapor) to form HF

$$4Si(s) + 2Cl_2\ (g) \text{ ---> } 4SiCl_4\ (g) + 130\ \text{kcal/mole}$$

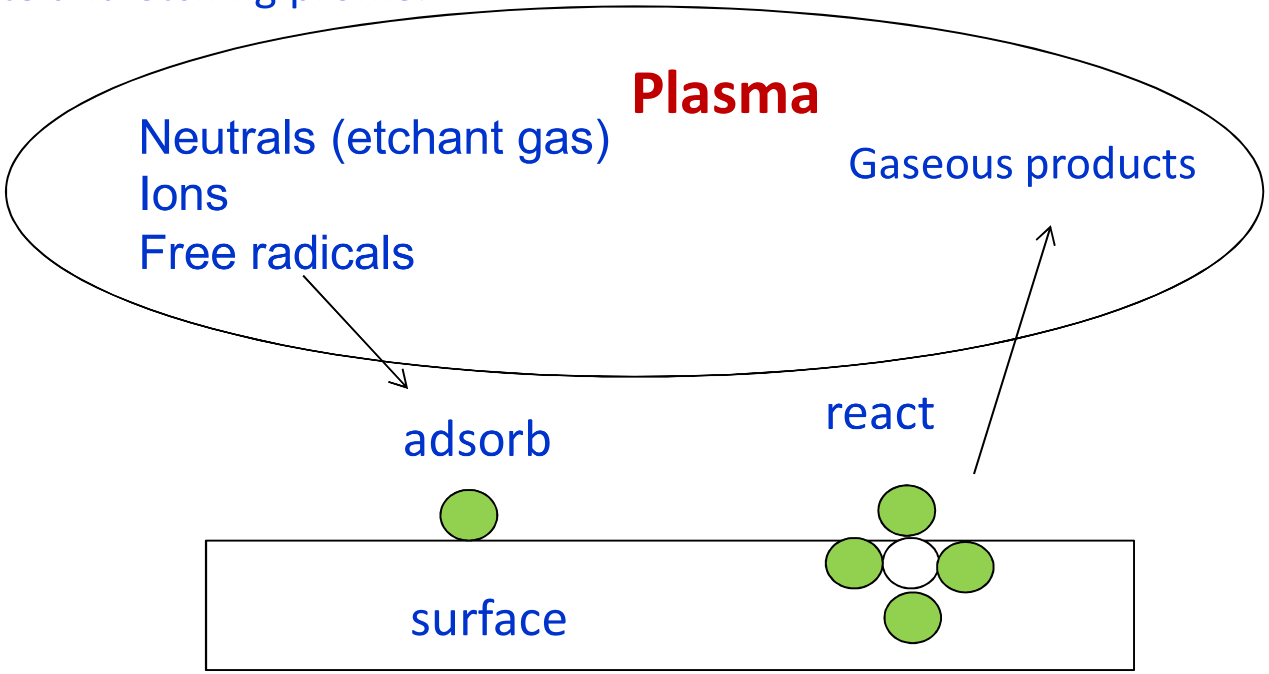
Although there is a large gain in free energy, the large activation energy does not allow low temperature processes - reaction is only effective above ~ 800°C.

In order to succeed with “gas” etching, one has to go out of equilibrium.

The solution is plasma etching.

# Plasma-based etching

- Directional etching due to presence of ionic species in plasma and (self-) biased electric field. (The self-bias electric field is not applied *externally*, but is created *spontaneously* in RF plasma)
- Two components exist in plasma
    - Ionic species result in directional etching.
    - Chemical reactive species result in high etch selectivity.
- Control of the ratio of ionic/reactive components in plasma can modulate the dry etching rate and etching profile.



**Plasma**

Neutrals (etchant gas)
Ions
Free radicals

Gaseous products

adsorb

react

surface

$$Si(s) + 4F(g) = SiF_4(g)$$

# RF plasma chemistry

For a plasma with inlet flow of molecule AB, Plasma processes are

**Dissociation**

$$e^* + AB \leftrightarrows A + B + e$$

**Atomic Ionization**

$$e^* + A \leftrightarrows A^+ + e + e$$

**Molecular Ionization**

$$e^* + AB \leftrightarrows AB^+ + e + e$$

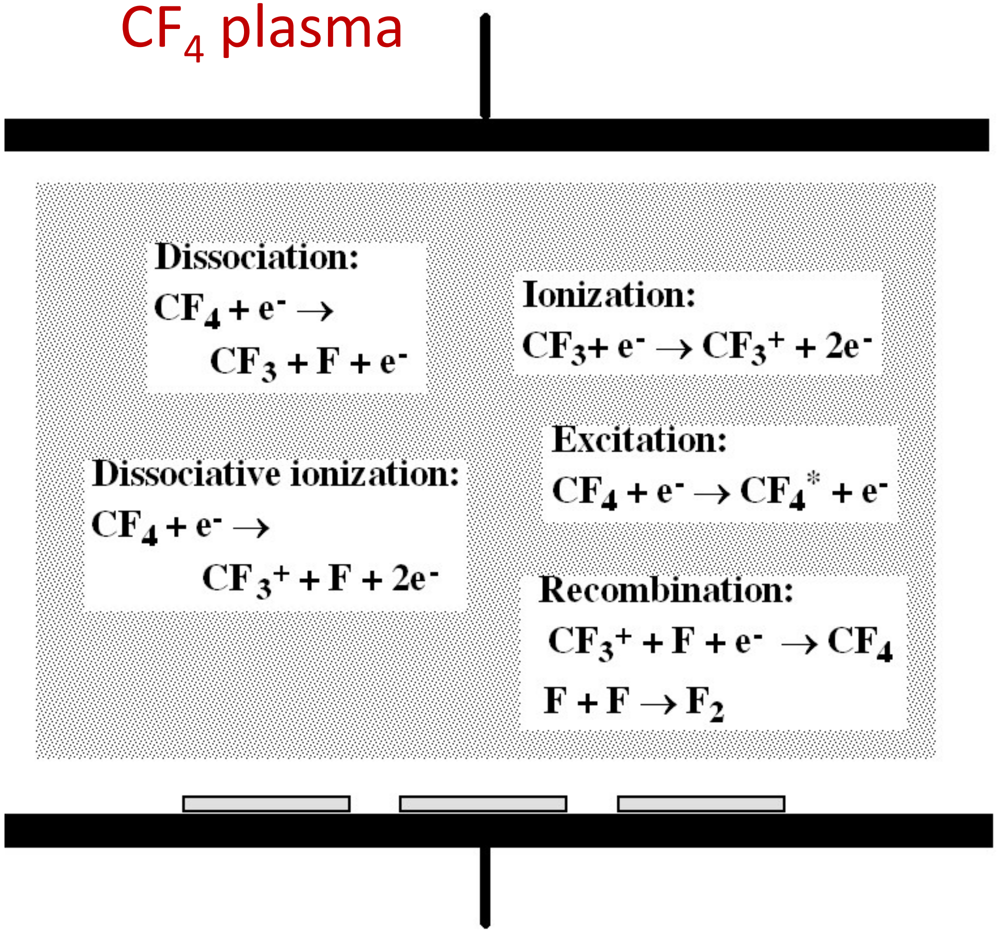
**Atomic Excitation**

$$e^* + A \leftrightarrows A^* + e$$

**Molecular Excitation**

$$e^* + AB \leftrightarrows AB^* + e$$

$CF_4$ plasma



**Dissociation:**

$CF_4 + e^- \rightarrow CF_3 + F + e^-$

**Ionization:**

$CF_3 + e^- \rightarrow CF_3^+ + 2e^-$

**Excitation:**

$CF_4 + e^- \rightarrow CF_4^* + e^-$

**Dissociative ionization:**

$CF_4 + e^- \rightarrow CF_3^+ + F + 2e^-$

**Recombination:**

$CF_3^+ + F + e^- \rightarrow CF_4$

$F + F \rightarrow F_2$

In equilibrium, degree of ionization typically $10^{-3}$ - $10^{-6}$, very low, meaning majority gas not ionized.

(plasma density = number of ions/cm$^3$ ~ typically $10^9 – 10^{13}$/cm$^3$.)

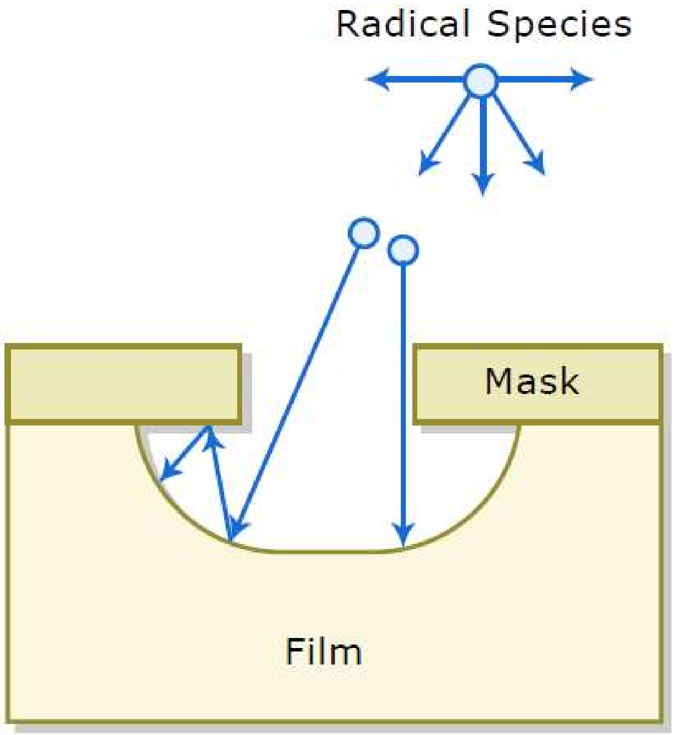
# Chemical etch: highly selective, but isotropic

- Due to their incomplete bonding (incomplete outer shells), free radicals (neutral, e.g. $CF_3$ and F from $CF_4$ plasma) are highly reactive chemical species.

$$e^- + CF_4 \rightarrow CF_3 + F + e$$

- Free radicals react with film to be etched and form vol

$$Si + 4F \rightarrow SiF_4$$



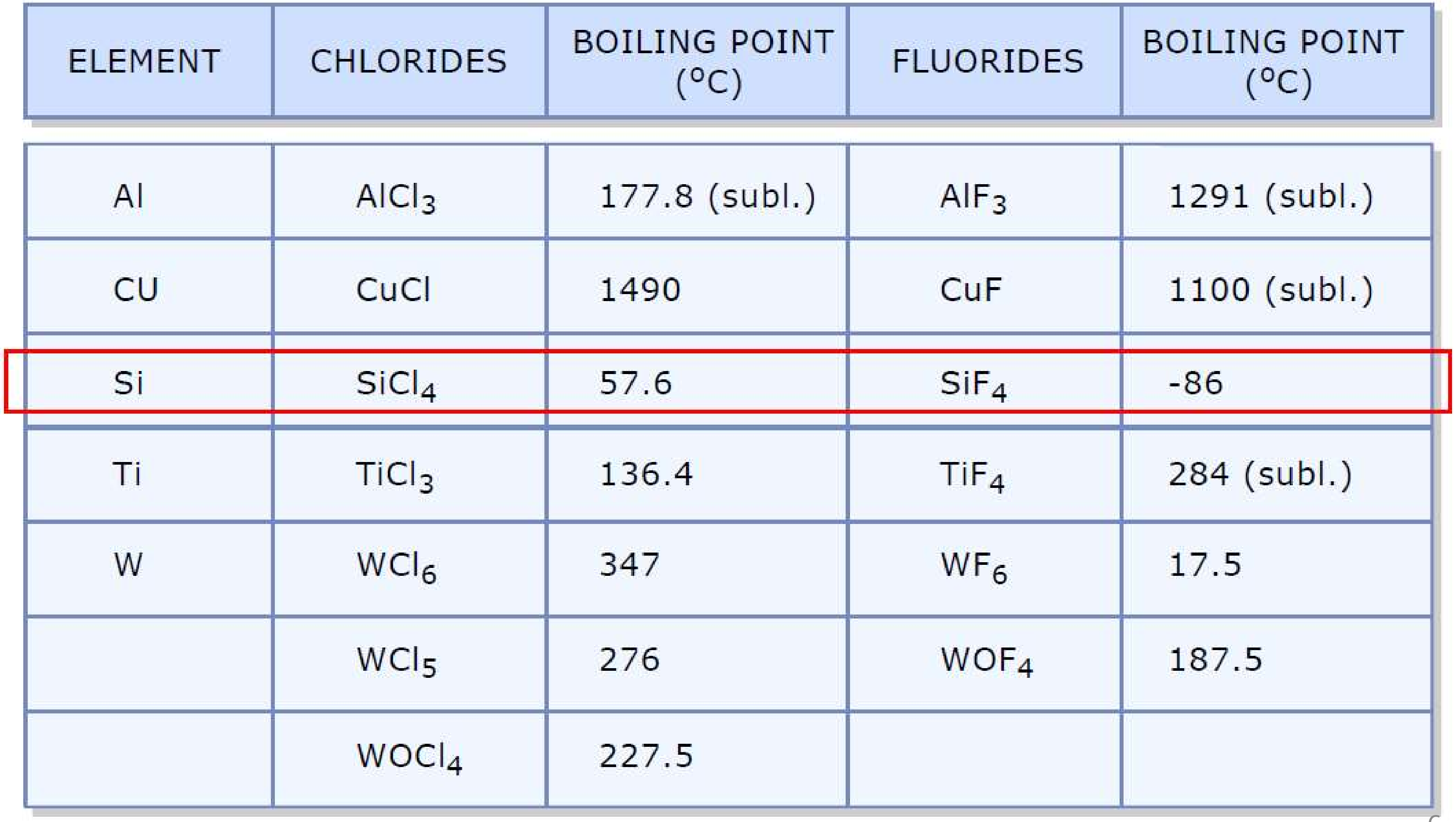
- Pure chemical etch is isotropic or nearly isotropic, and the etching profile depends on arrival angle and sticking coefficients of free radicals.
- Free radicals (un-charged) in plasma systems have isotropic arrival angles.
- The sticking coefficient S is very low, typically only S~0.01 (i.e. most free radicals adsorb then just bounce back without reaction).
- This leads to isotropic character of etch, as free radicals can etch area beneath the mask due to bouncing, as seen in the figure. The resulted profile has large undercut.

# Etch byproducts should have low boiling point

Low boiling point means very volatile, so it can be pumped away.

This is not necessary for *physical* etching/sputtering, where etch product is sputtered off that ideally doesn’t fall on the other part of the wafer (re-deposition).

Boiling points of typical etch products

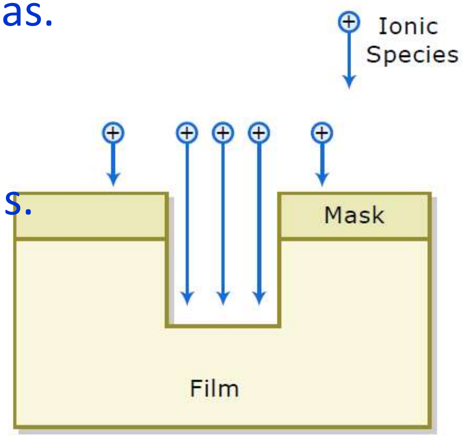


| ELEMENT | CHLORIDES | BOILING POINT (°C) | FLUORIDES | BOILING POINT (°C) |
|---|---|---|---|---|
| Al | $AlCl_3$ | 177.8 (subl.) | $AlF_3$ | 1291 (subl.) |
| CU | CuCl | 1490 | CuF | 1100 (subl.) |
| Si | $SiCl_4$ | 57.6 | $SiF_4$ | -86 |
| Ti | $TiCl_3$ | 136.4 | $TiF_4$ | 284 (subl.) |
| W | $WCl_6$ | 347 | $WF_6$ | 17.5 |
|  | $WCl_5$ | 276 | $WOF_4$ | 187.5 |
|  | $WOCl_4$ | 227.5 |  |  |

# Physical etch component in a plasma etch system (much less important than chemical etch)

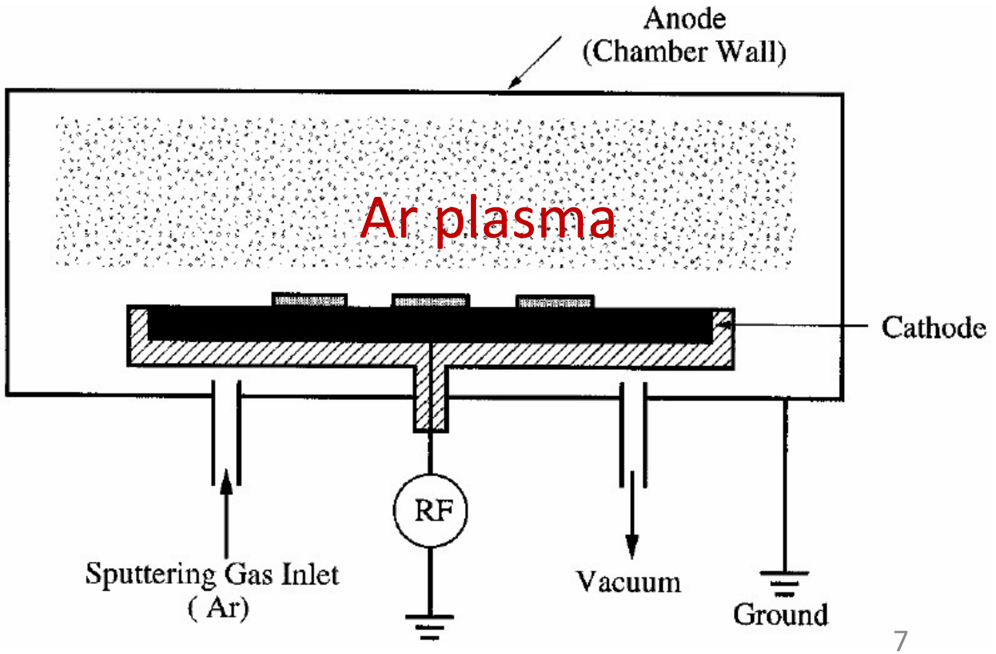
1. Ionic species are accelerated toward each electrode by built-in self-bias.
2. The ionic species strike wafer surface and remove the material to be etched.
3. Directional, non-selective - similar sputter yield for different materials.

   It may result in significant re-deposition.

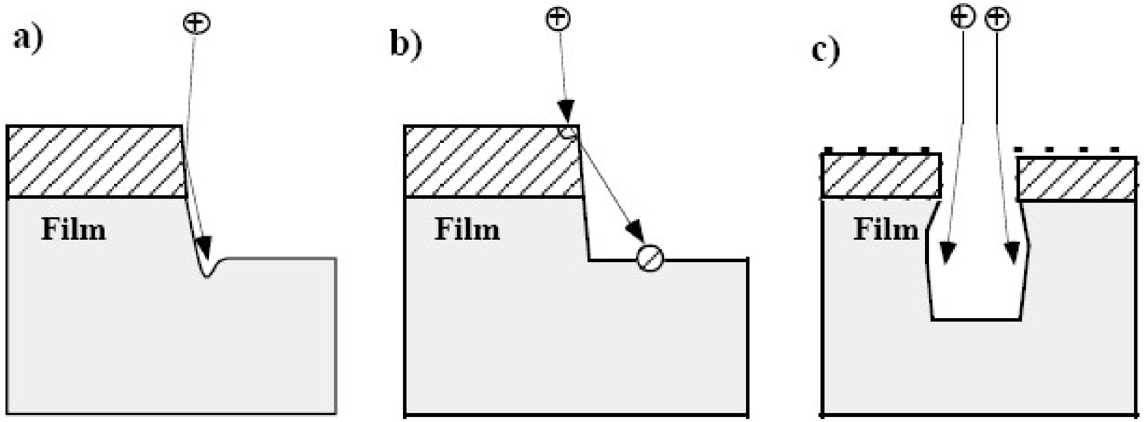


Pure physical etch: sputter etching system

- Self-bias few 100V, but low ion energy (order 10V) due to collision energy loss.
- Thus very low milling rate in a sputter system, often for surface cleaning only.
- For a dedicated ion milling system (no plasma, see later slides), the pressure is ~$10^{-4}$Torr or even lower (cannot sustain a plasma), leading to large mean free path, high ion energy and high milling rate.



# Sputter etching and ion milling



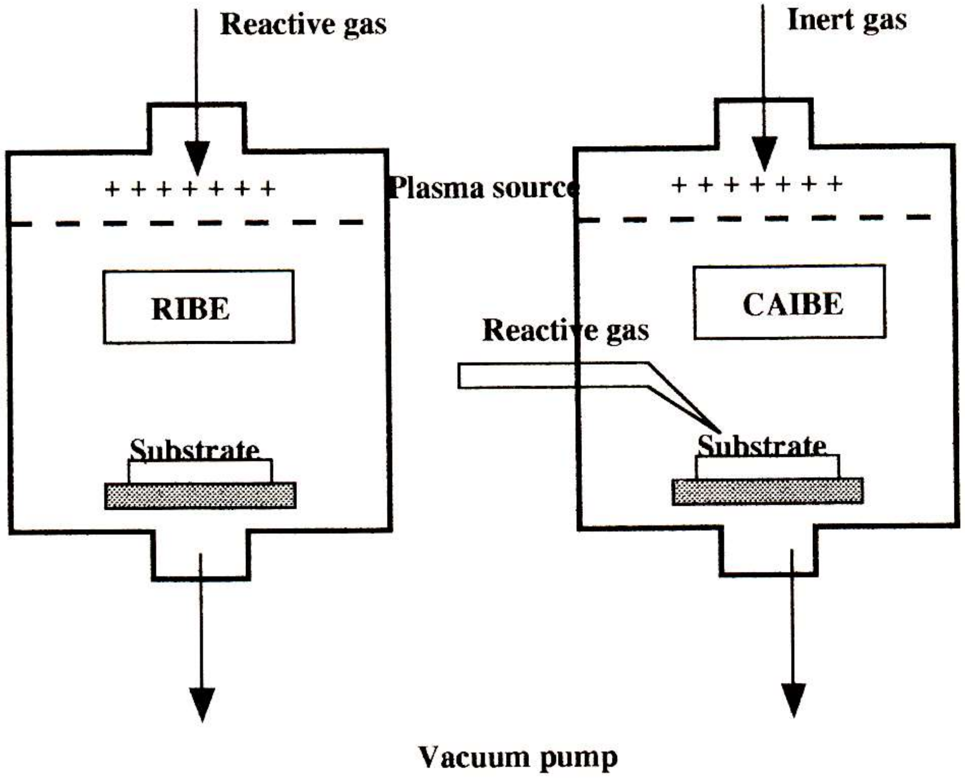
Problems associated with sputter etching (or any etching that has a high degree of physical/ionic etching):

a) trenching at bottom of sidewalls;

b) redeposition of photoresist and other materials;

c) charging and ion path distortion.

# Chemically assisted ion beam etching system

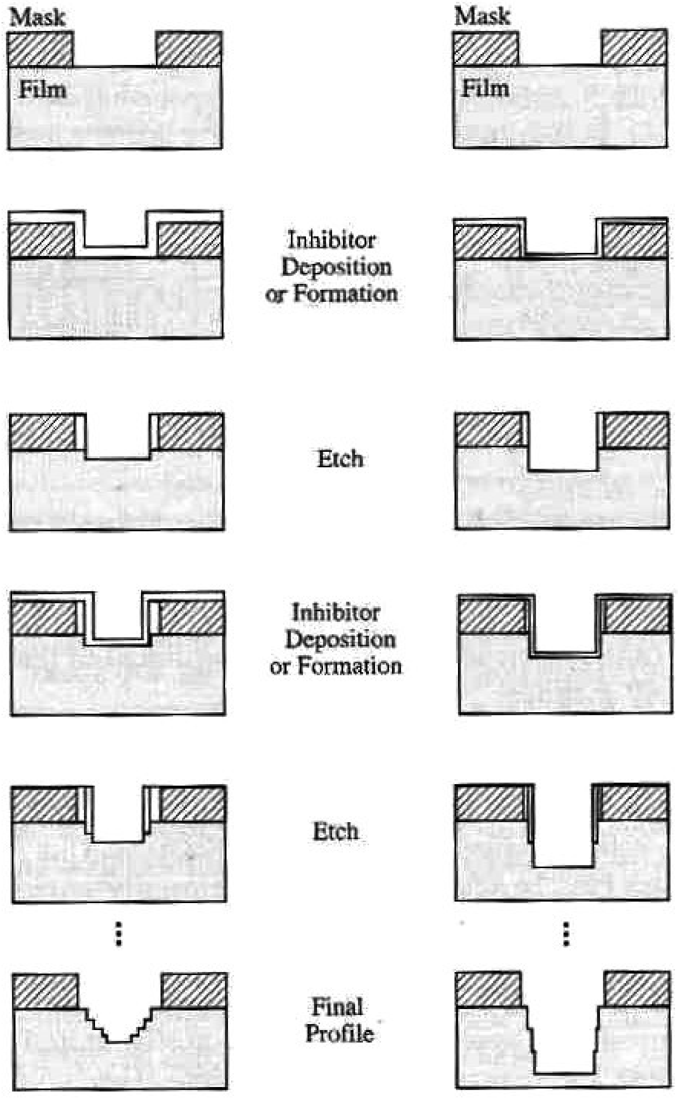


- RIBE: reactive IBE, reactive gases are introduced into plasma region together with Ar gas, so they are ionized. RIBE is virtually the only example where the same ion has both a physical (ion impact) and chemical (reactive etching) component.
- CAIBE: chemically assisted ion beam etching, inert Ar ion, neutral reactive gas is introduced into lower chamber, so not ionized, though some may be ionized due to backflow into plasma region or bombardment by Ar ion.

# Example:
# etching profile of Si or $SiO_2$

High inhibitor deposition rate

Low inhibitor deposition rate

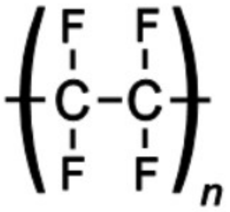


a. Inhibitor deposition rate fast compared to etch rate

b. Inhibitor deposition rate relatively slow compared to etch rate

Figure 10-14

Teflon



$-(CF_2-CF_2)_n-$

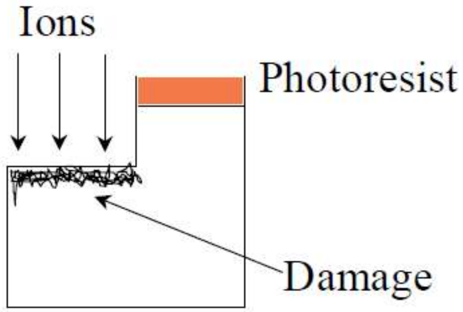
- Fluoropolymer (like Teflon) in $CHF_3$ or $CF_4$+$H_2$ RIE of Si or $SiO_2$ is the inhibitor.
- If Ar gas is added, inhibitor is mainly removed by ion bombardment. So less attack of inhibitor on sidewall.
- If $O_2$ gas is added, inhibitor on sidewall is removed at faster rate than Ar ion, but the etch of inhibitor at horizontal surface is even faster.
- Yet at very low temperature, inhibitor $SiO_xF_y$ (not act as inhibitor at higher temperature when it is volatile) forms when $O_2$ is added, which is the mechanism for fast anisotropic etching of Si using cryo-etcher. (deep Si etcher, popular for MEMS – micro electro mechanical systems)

# Anisotropy due to ion bombardment: summary

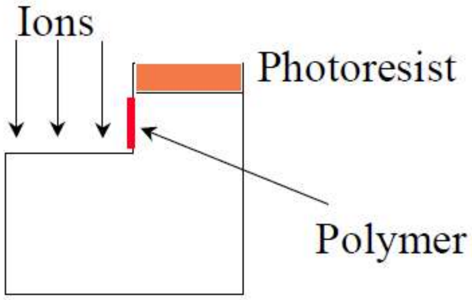
- Due to its extremely low density, ions don’t contribute much to etching; neutral radicals do.
- So even with directional ion bombardment, the overall etching can still be pretty isotropic.
- For instance, $SF_6$ etch of Si is very isotropic with large undercut like wet etch.
- To achieve anisotropy, there are two mechanisms:
  - Energy-driven anisotropy: bombardment by ion disrupts an un-reactive substrate and causes damages such as dangling bonds and dislocations, resulting in a substrate more reactive towards etchant species (electron or photon can also induce surface activation).
  - Inhibitor-driven anisotropy: ion bombardment removes the inhibitor layer from horizontal surface (sidewall remain passivated), and reaction with neutrals proceed on these un-passivated surfaces only.

One may think that ions won’t help much due to its much lower density than radicals. But ion has sticking coefficient S~1 (every ion bombardment counts), whereas radicals S~0.01 (most radicals hit the surface and left without doing anything).

Energy-driven anisotropy



speeds chemical reaction
on horizontal surfaces.

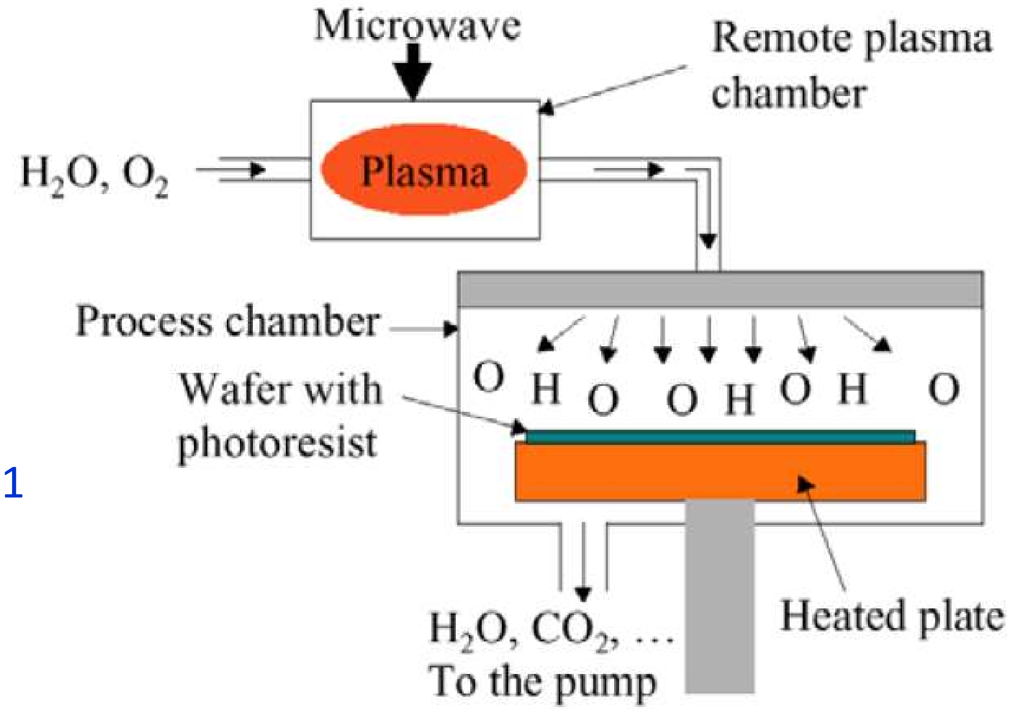


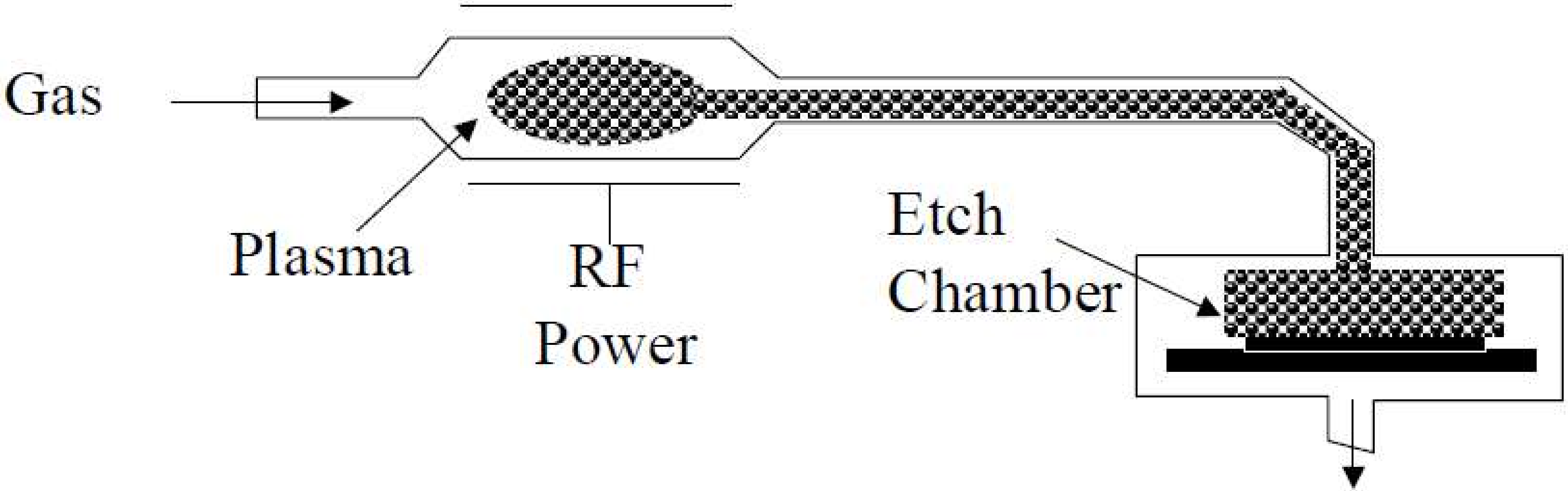
slows chemical reaction
on vertical surfaces.

Inhibitor-driven anisotropy

# Downstream etchers

- Plasma is formed in a cavity which is separated from the etching chamber.
- Wafers are shielded from bombardment.
- Only neutral free radicals reach wafers.
- Etching is completely chemical and isotropic.
- High selectivity achievable - Si:SiO2 = 50:1
- Plasma may be generated by RF (13.56MHz) or by microwave (2.45GHz).

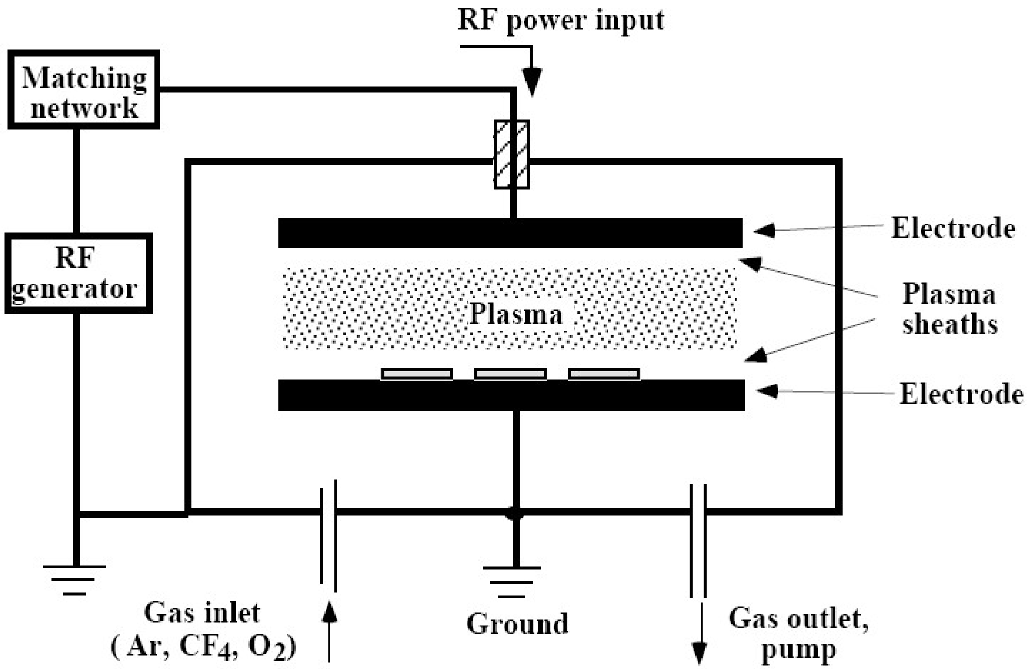




# Plasma etching in parallel plate systems – plasma mode

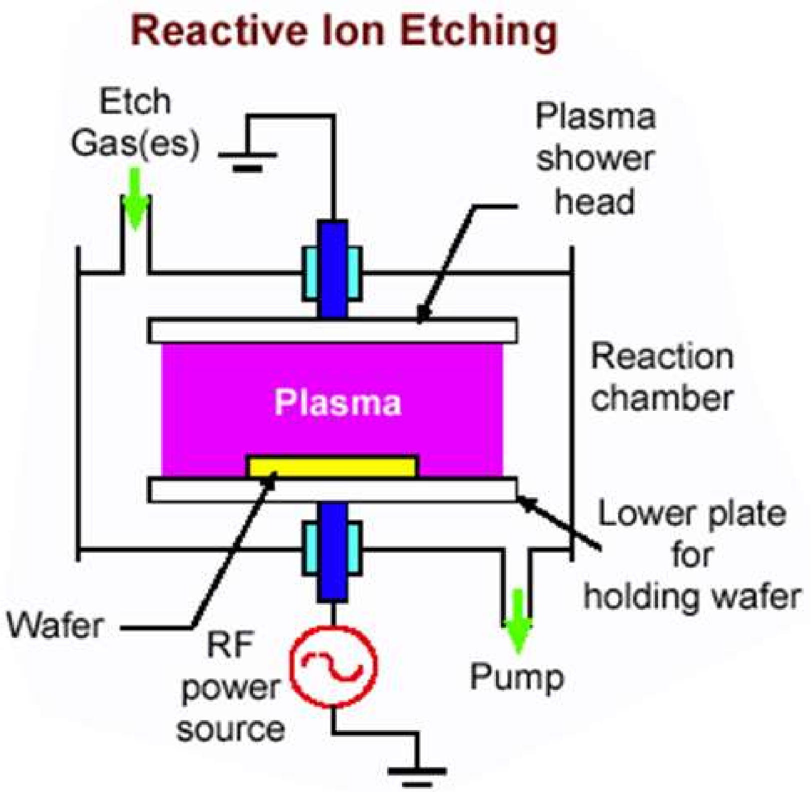
Parallel plate = capacitively coupled plasma (CCP)

- Both chemical and physical etch occur (wafer "in contact" with plasma), though the later is weak, particularly at higher pressure when DC voltage drop near wafer is smaller.
- Etching is fairly isotropic and selective due to the strong chemical component.



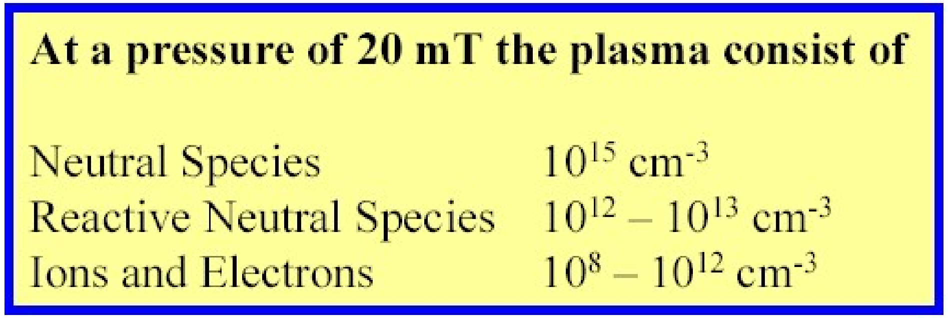
# Parallel plate etchers (regular RIE, low density plasma)

- Absolutely the most important form of dry etching, though recently ICP (see later slides) is becoming more and more popular.
- Compared to plasma mode: smaller wafer electrode (*counter electrode* grounded to chamber wall), lower pressure (<100mTorr), more physical bombardment (voltage drop many 100V).
- Ion enhanced etching mechanism, (usually) directional/anisotropic and selective.



RIE using parallel plate setup is low density plasma system (ions $10^8$ – $10^{10}$/cm$^3$), thus low etch rate.

Here low (ion) density plasma also implies low density of free radicals. Thus low etching rate.



**At a pressure of 20 mT the plasma consist of**

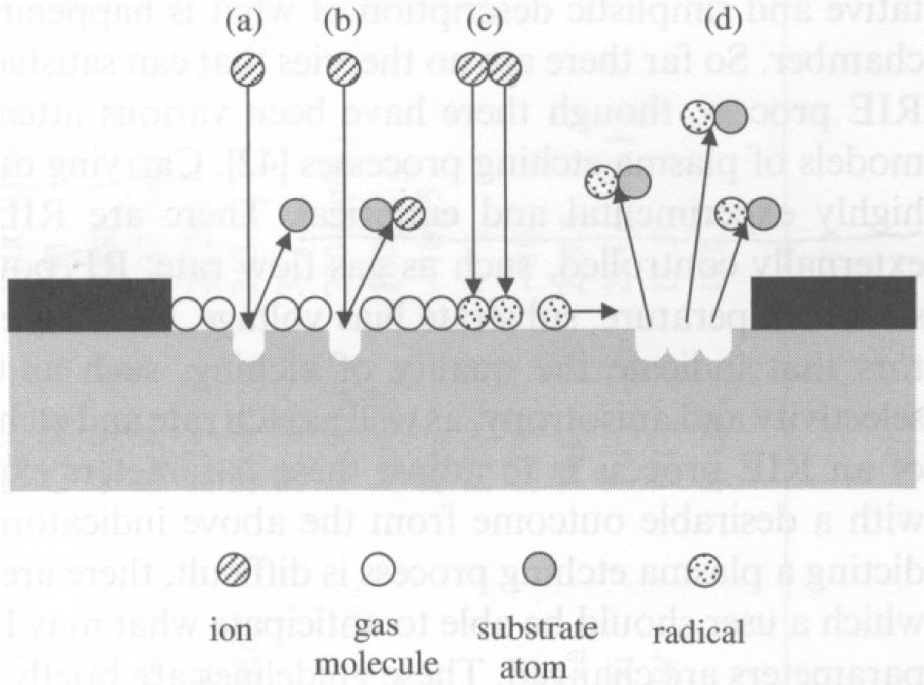
| | |
|---|---|
| Neutral Species | $10^{15}$ cm$^{-3}$ |
| Reactive Neutral Species | $10^{12}$ – $10^{13}$ cm$^{-3}$ |
| Ions and Electrons | $10^{8}$ – $10^{12}$ cm$^{-3}$ |

VERY roughly, one can say that plasma consists of order 1% radicals (reactive neutral species) and 0.01% ions.

# Reactive ion etch (RIE)

- Due to its simultaneous anisotropy and selectivity, RIE is intensively used.
- Works for most semiconductors and dielectrics.
- OK for few metals that form volatile etch products: Al (form $AlCl_3$), Cu ($CuCl_2$) (not really), Ti ($TiF_4$, $TiCl_4$), W ($WF_6$), Cr ($CrO_2Cl_2$).

Schematic RIE process

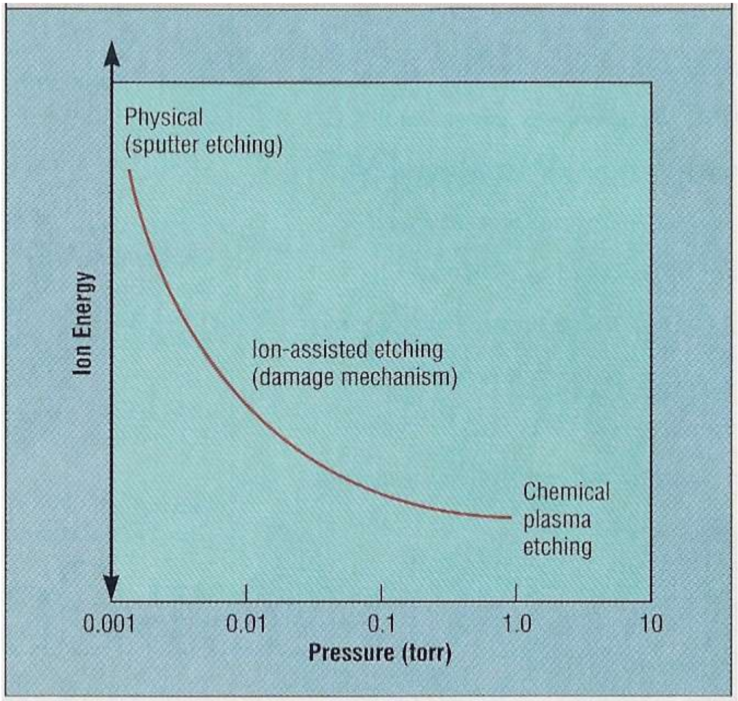


a) Ion sputtering, b) reactive ion etching, c) radical formation (?), d) radical etching (most important)

In RIE, ion energy is low (several 10s eV, << voltage drop near wafer surface, due to collision energy loss), and its number density is very low, thus negligible etching by ion bombardment.

The name reactive "ion" etching is very misleading since ions don't contribute *directly* to etching – it just "helps" chemical etching.

# Ion energy vs. pressure for a plasma



Ion Energy vs. Pressure for a plasma.

- Lower pressure (<10mTorr) increases mean free path as well as voltage drop near wafer electrode, both of which leads to more energetic and directional ion bombardment, thus more anisotropic, but less selective and slower etching rate due to low ion/free radicals density.
- High pressure (>100mTorr), short mean free path, low voltage drop, isotropic chemical etching.
- Thus it is desirable to have a low pressure plasma with high ion density.

Plasma mode: >100mTorr

RIE mode: 10-100mTorr

Sputter etching: pressure as low as possible, as long as plasma can be sustained, but still very slow etching rate.

# Electron cyclotron resonance (ECR) and inductively coupled plasma (ICP)

ECR was introduced in 1985.

ICP was introduced much later (1991- 1995).

Dual plasma source:

Top one (ECR or ICP RF power) generates HDP, determines ion density/current.

Bottom one (CCP RF power) generates bias voltage like regular RIE, determines ion energy.

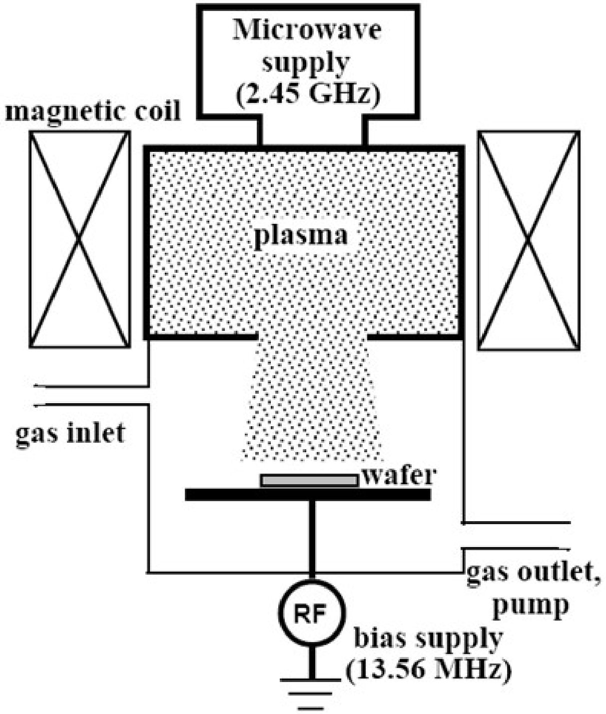
Typical parameters for HDP and conventional plasma etcher

| Parameters | RF Etcher | HDP Etcher |
|---|---|---|
| Pressure (mT) | 50~1000 | 0.5~50 |
| Plasma Density ($cm^{-3}$) ions/$cm^3$ | $10^9$~$10^{11}$ | $10^{10}$~$10^{12}$ |
| Ion Energy (eV) should be lower | 200~1000 | *Controllable* 20~500 |
| Ion Current Density ($mA/cm^2$) | 0.1~2 | 1~20 |
| Electron Temperature (eV) | 1~5 | 2~7 |
| Ionization rate | $10^{-6}$~$10^{-3}$ | $10^{-4}$~$10^{-1}$ |

CCP: capacitively coupled plasma, parallel plate, used for conventional regular RIE.

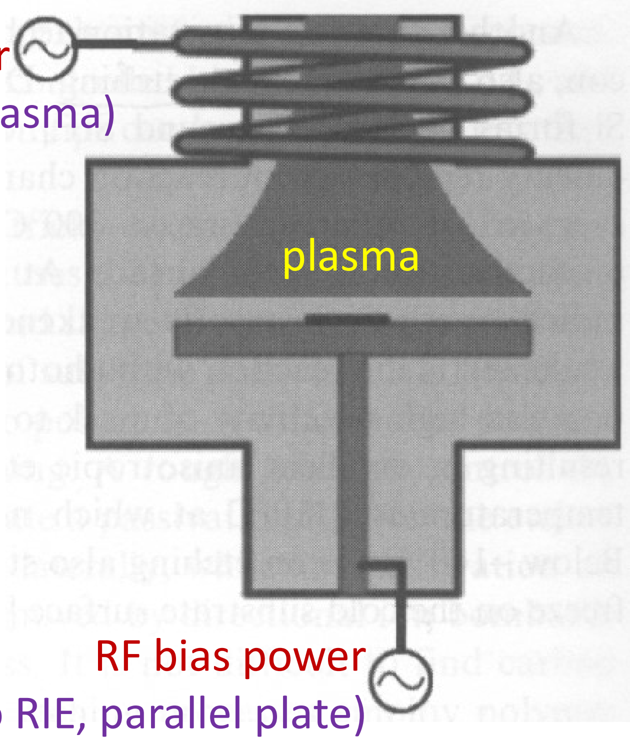
# ECR and ICP

## Electron cyclotron resonance plasma
(less common nowadays)



## Inductively coupled plasma (ICP)

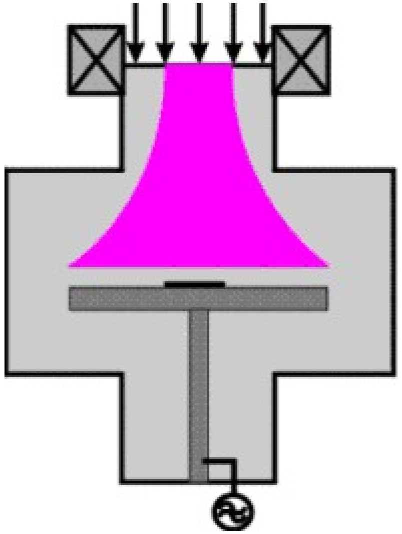
ICP RF power
(for dense plasma)

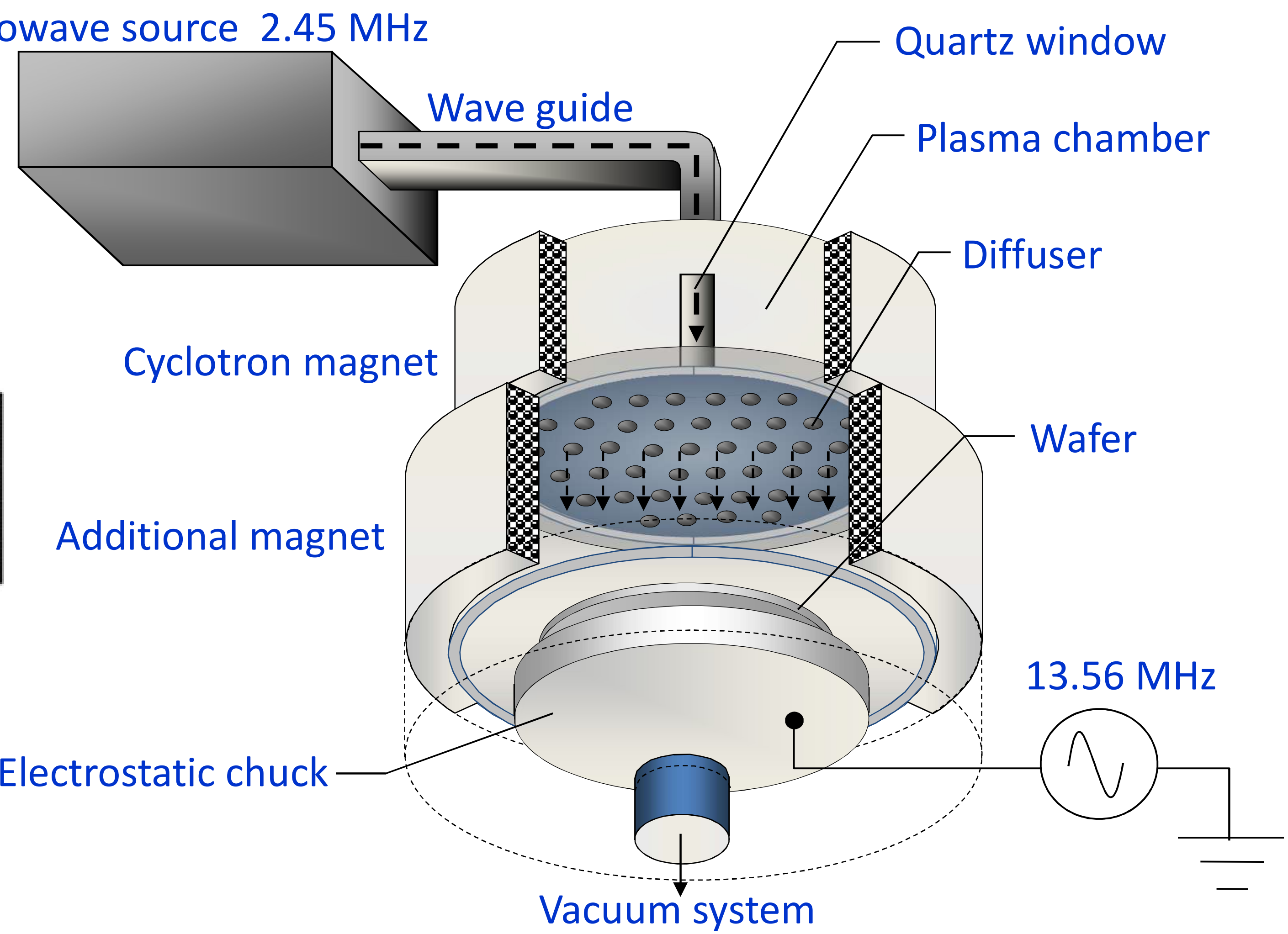


RF bias power
(similar to RIE, parallel plate)

- High magnetic field in the coil, so electrons move in circles with long path, leading to higher collision and ionization probability, and much less electron loss to chamber wall and the bottom plate where sit the wafer. Moreover,
- For ICP, AC magnetic field induces circular electrical field, which accelerates electrons.
- For ECR, DC magnetic field, electron cyclotron $\omega = qB/m$; electrons accelerated if this frequency matches the microwave frequency.

# Schematic of ECR etcher





Microwave source 2.45 MHz

Wave guide

Quartz window

Plasma chamber

Diffuser

Cyclotron magnet

Wafer

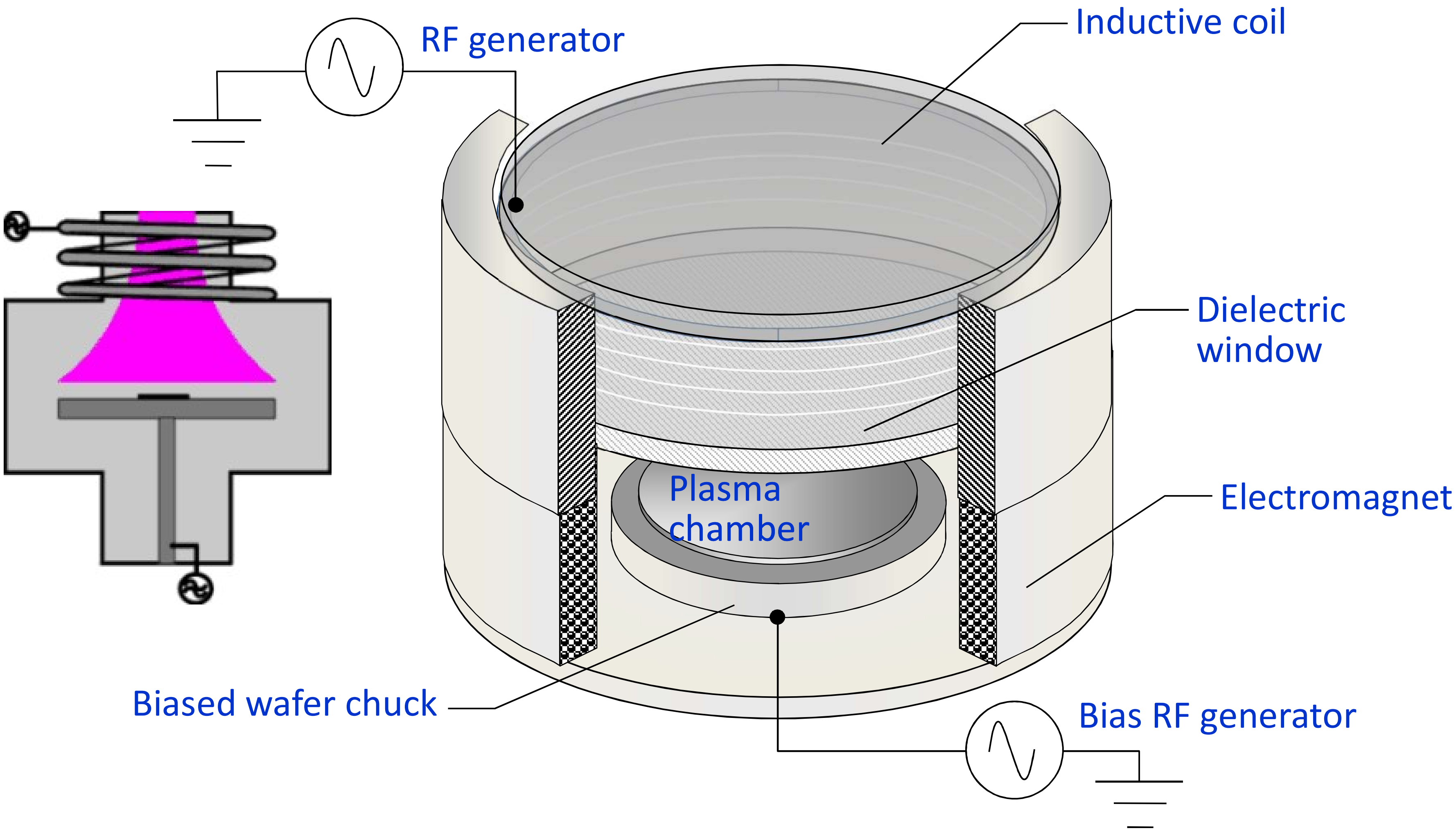
Additional magnet

13.56 MHz

Electrostatic chuck

Vacuum system

# Schematic of ICP etcher

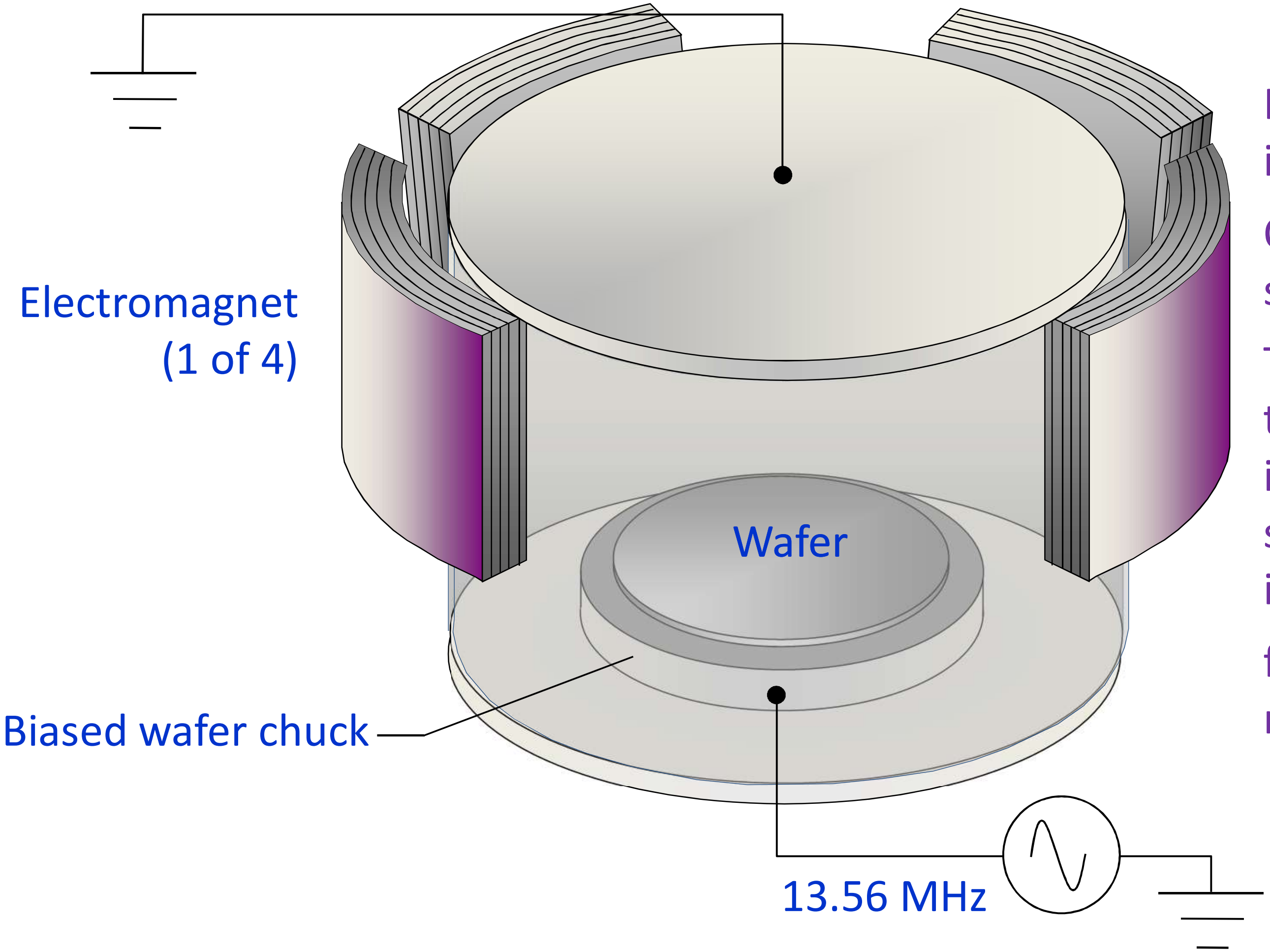


As you see, there is practically no top plate as in parallel plate regular RIE.
The wafer sees the ICP power – the two power sources are not physically separated.
Otherwise, even though the plasma density in the upper part is high, it will get lost due to re-combination and de-excitation when it travels through the bottom part.

# Magnetically enhanced reactive ion etch (MERIE)

Like regular parallel plate RIE, but magnetic field forces electron to go circles, increasing collision with gas molecules and decreasing loss to chamber walls or top/bottom plates.

However, now that electrons don’t loss to bottom plate, no or little bias voltage – need to apply an external bias to accelerate ions.



I haven’t seen any MERIE, so it is not popular.

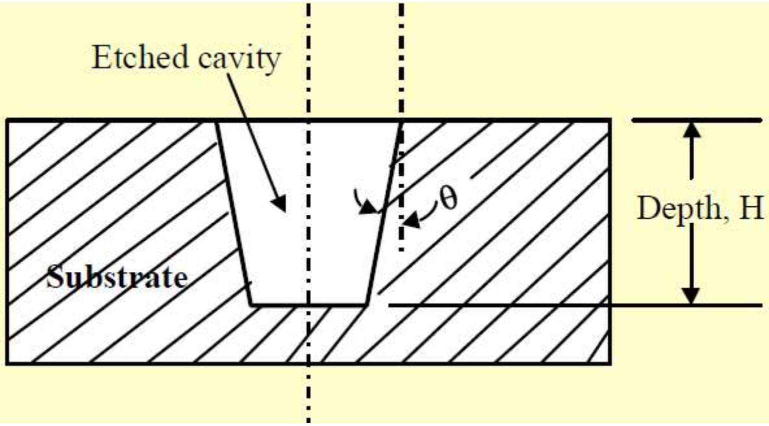
On the contrary, magnetron sputtering is very popular.

This is probably because there are many ways to increase etching rate; but sputter without magnetron is always very slow:

few nm/min, vs. 10s to 100s nm/min RIE etching rate.

# Why deep RIE (DRIE)?

- Plasma etching can produce deeper trenches than wet etching, but with tapered angles.
- Tapered trenches are not desirable in many applications such as resonators that involve pairs of “centipedes-like” micro-devices with overlapped “fingers”.
- DRIE process may produce deep high aspect ratio structures with vertical sidewall (θ ≈ 0°).
- It is the most important breakthrough in drying etching in recent years, popular for MEMS (micro electro mechanical systems) fabrication.



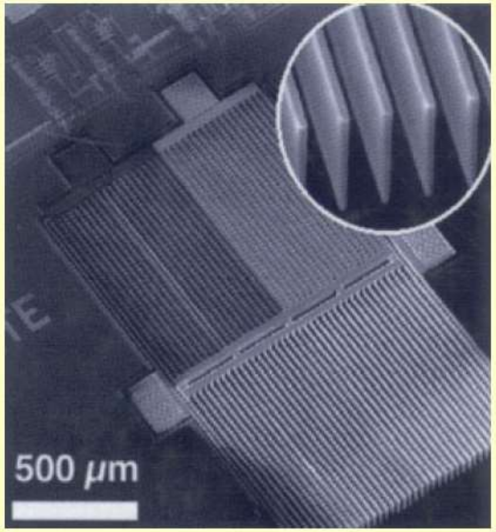
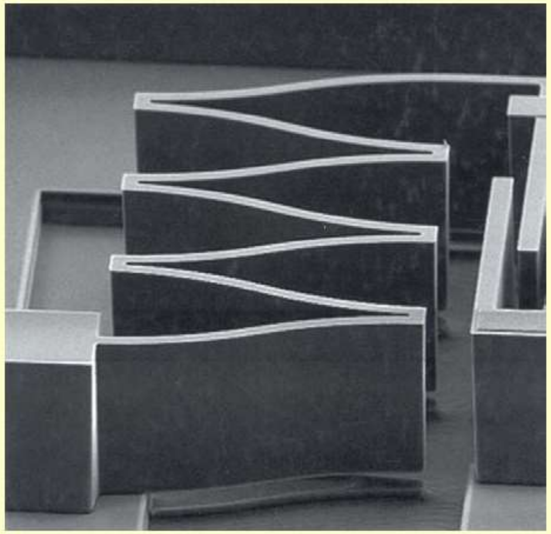


**Plate- resonators**



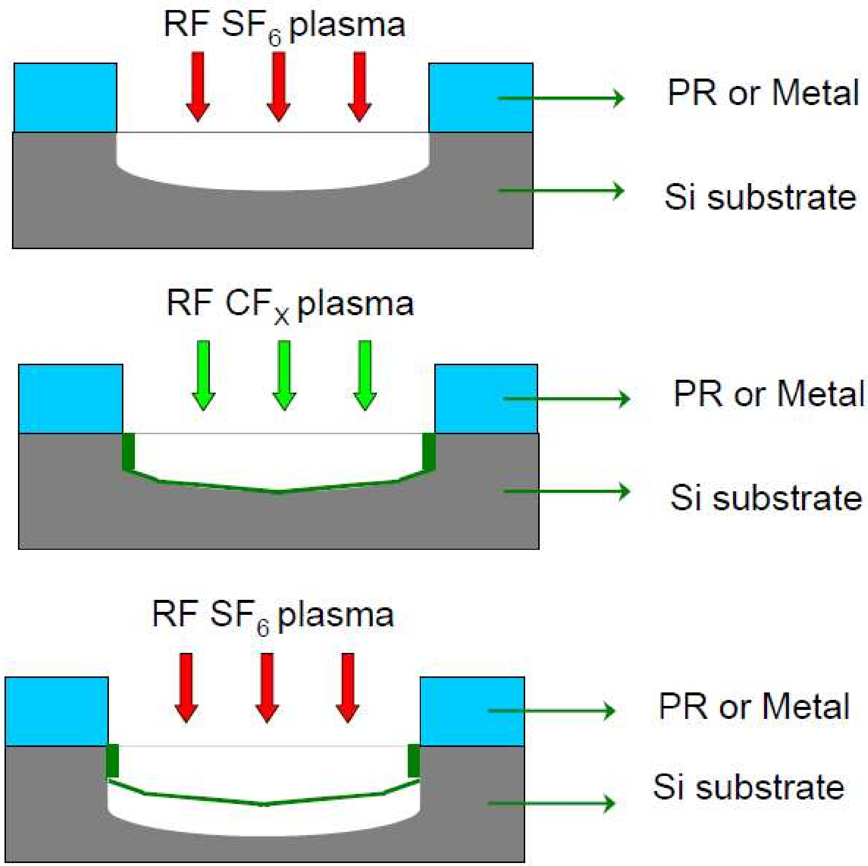
**Spring resonator**

Working principle:

- The DRIE process provides thin film of a few microns protective coating on the sidewalls during the etching process.
- It involves the use of a high-density plasma source.
- The process allows alternating process of plasma (ion) etching of the substrate material and the deposition of etching-protective material on the sidewalls.

# Deep Si etch: ICP - “Bosch” process

ICP: inductively coupled plasma
ECR: electron cyclotron resonance



Besides Bosch process, the other very popular deep Si etch is *cryo-etch* (i.e. at very low temperature, order -100°C, $SiO_xF_y$ as inhibitor). Often a deep RIE tool can do both processes.

- Uses high density plasma (ICP is used, but ECR also works) to alternatively etch silicon and deposit an etch-resistant polymer on sidewalls.
- $SF_6$ etch 5-13 sec; followed by $C_4F_8$ fluorocarbon polymer deposition 5-10 sec.
- Etch rate several $\mu$m/min, capable of etching several hundred $\mu$m with vertical walls.
- Sidewall is rough, depending on cycle times (longer cycle, more zigzag).
- Process recipe depends on geometry (aspect ratio…).
- More popular for MEMS, less common for nano-fabrication due to sidewall zigzag.

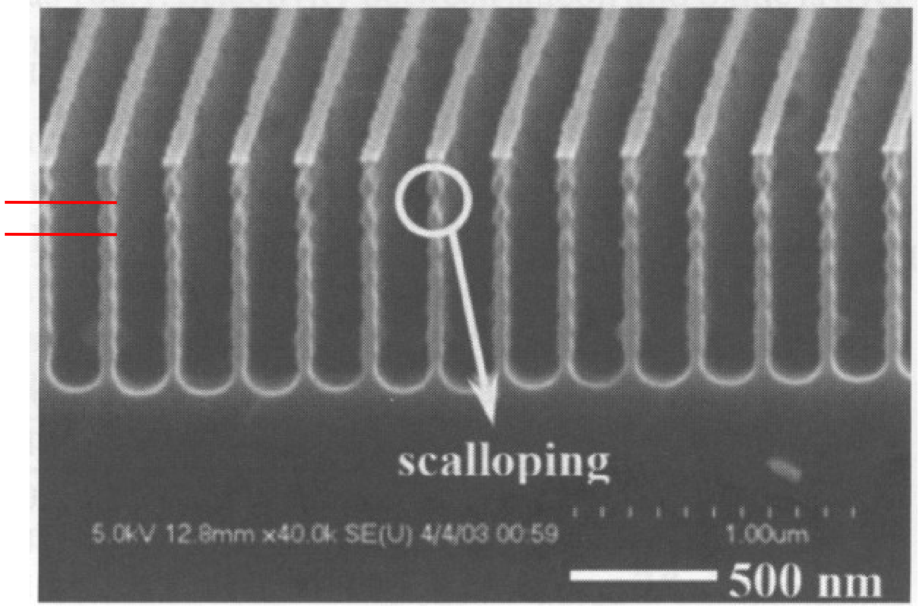
# Deep Si etch - Bosch process

DRIE uses lower energy ions → less damage and higher selectivity.

Plasma maintained at 0.5 to 3mTorr.

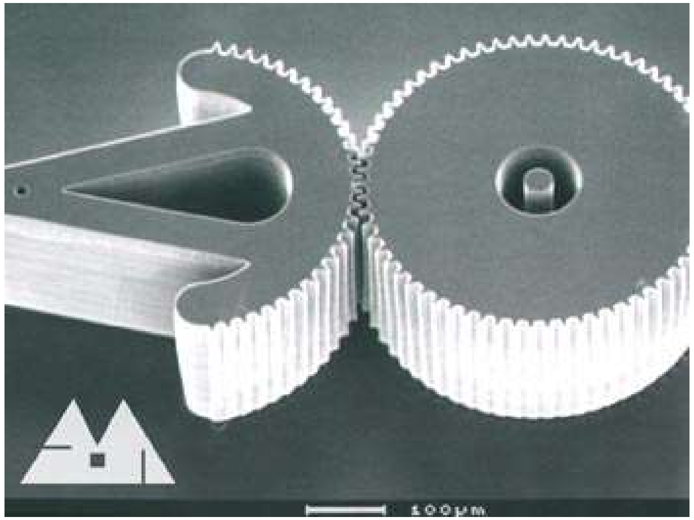
Rough sidewall due to scalloping effect.

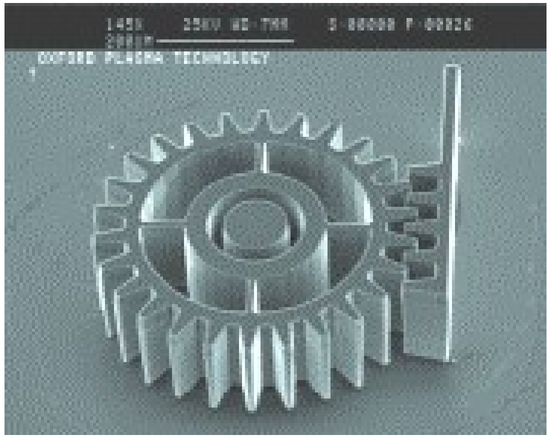
1 cycle

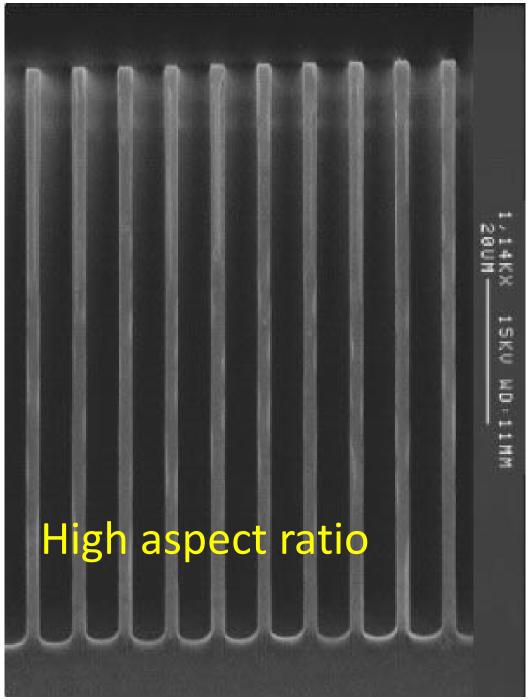


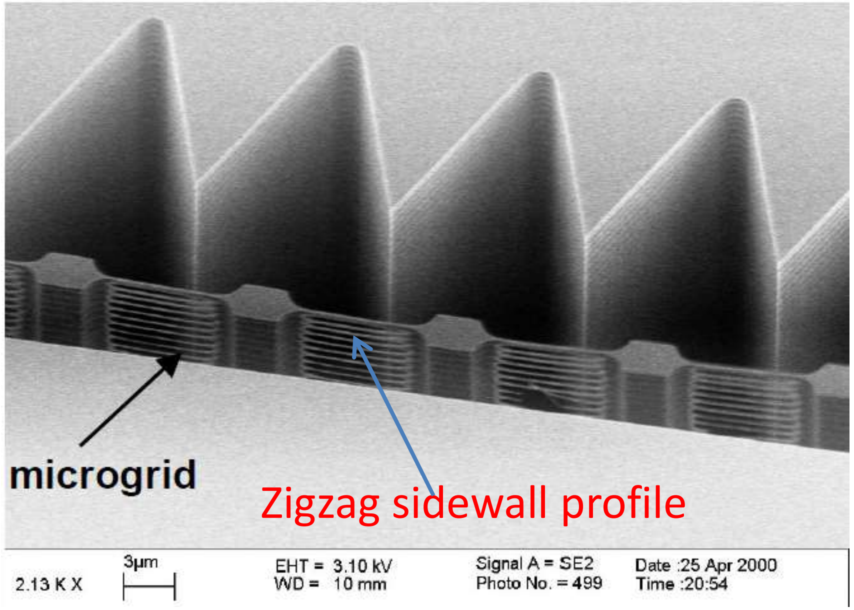
20 $\mu$m deep pores

# More examples of deep Si etch

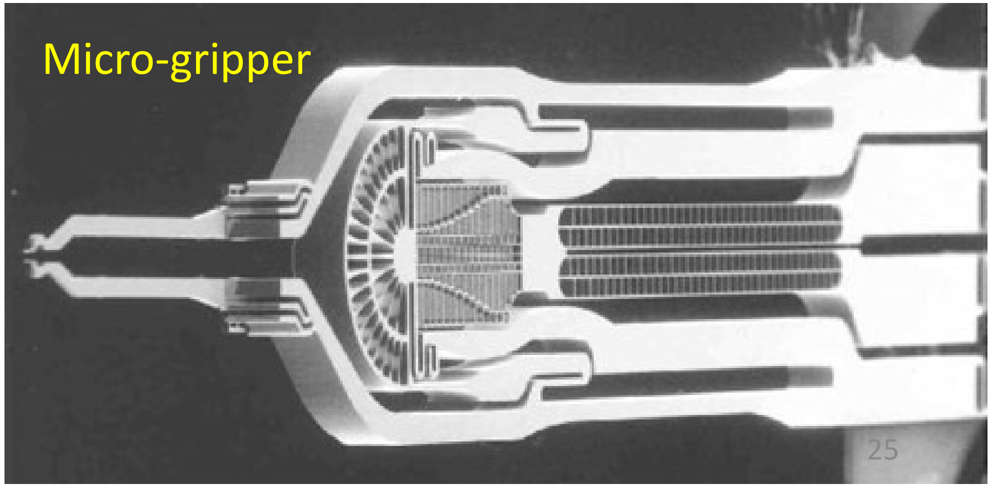




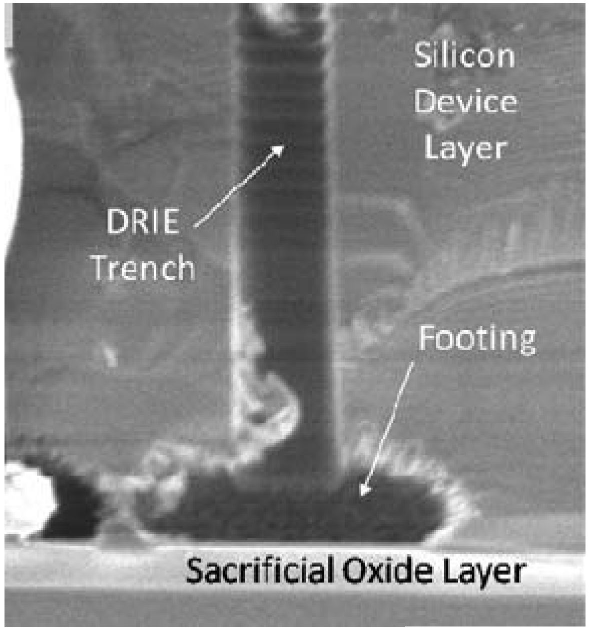

High aspect ratio


microgrid

Zigzag sidewall profile

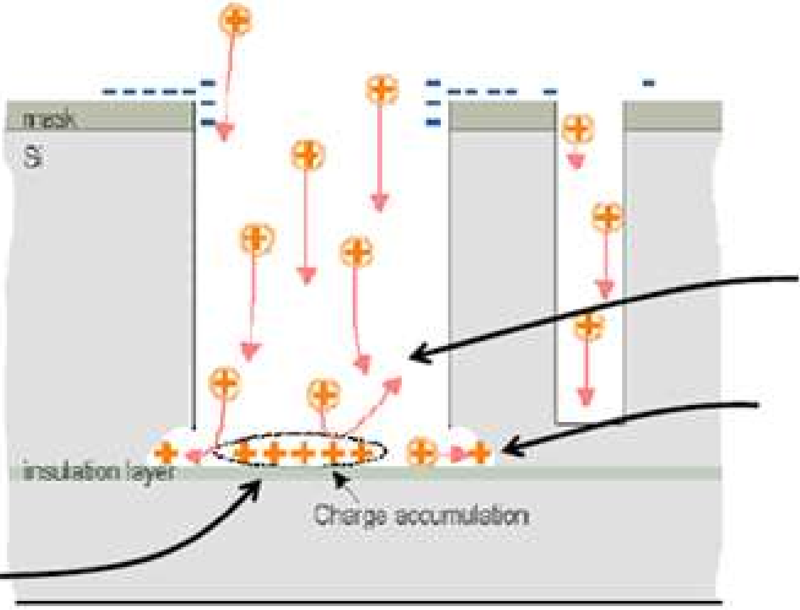

Micro-gripper

# DRIE issues: “footing”



Due to 200:1 selectivity, the (vertical) etch practically just stops when it reaches $SiO_2$ stop layer.

Problem: lateral undercut at $Si/SiO_2$ interface → “footing” caused by charge accumulation at the insulator.



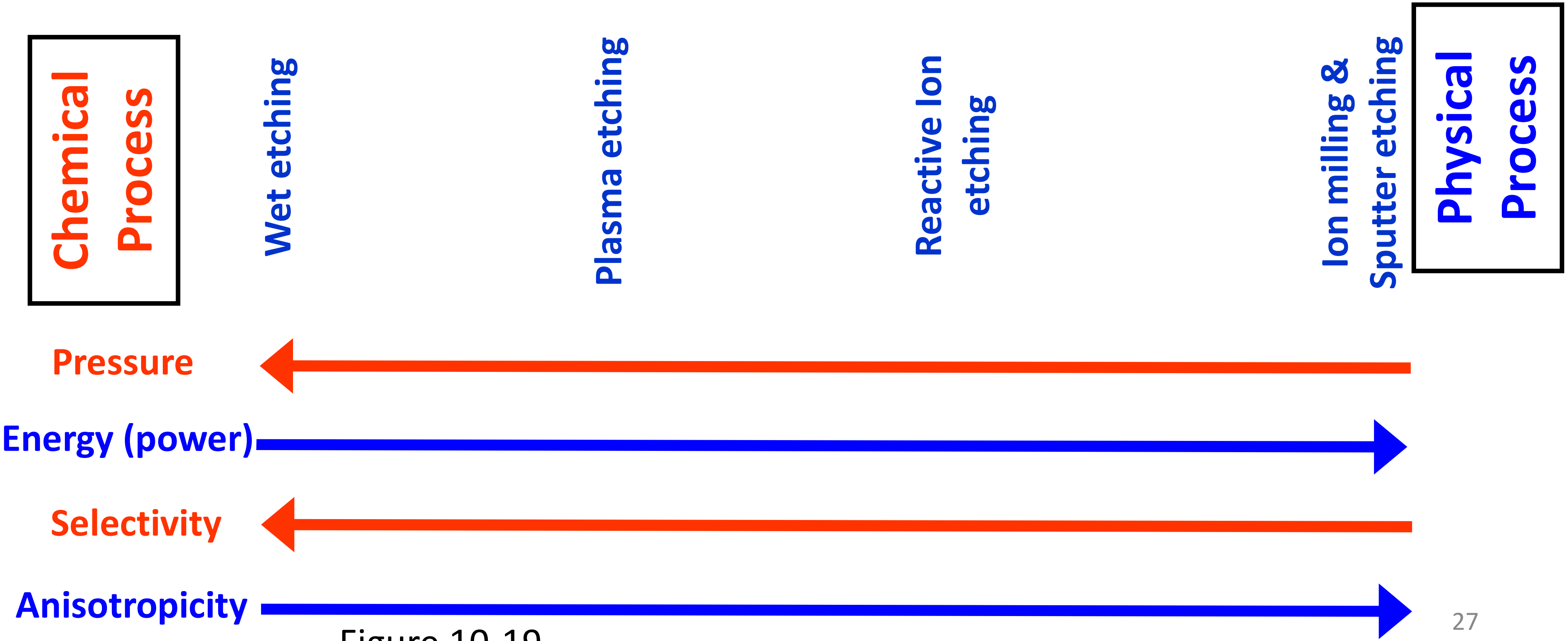
Poor charge relaxation and lack of neutralization by electrons at insulator leads to ion flux into substrate builds up positive potential.

Charging-induced potential perturbs the electric field, distorts the ion trajectory.

Result: strong and localized damage (“footing”) to the structure at Si-SiO2 interface.

# Summary: plasma etching mechanism

- Chemical etching: free radicals react with material to be removed. E.g. plasma etching at high pressure close to 1Torr.
- Physical etching or sputtering: ionic species, accelerated by the built-in electric field (self-bias), bombard the materials to be removed. E.g. sputter cleaning using Ar gas in sputter deposition system.
- Ion enhanced etching: combined chemical and physical process, higher material removal rate than each process alone. E.g. reactive ion etching (RIE), which is the most widely used dry etching technique.



**Chemical Process**

**Wet etching**

**Plasma etching**

**Reactive Ion etching**

**Ion milling & Sputter etching**

**Physical Process**

**Pressure**

**Energy (power)**

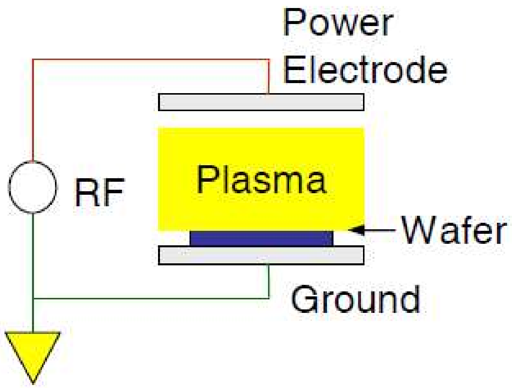
**Selectivity**

**Anisotropicity**

Figure 10-19

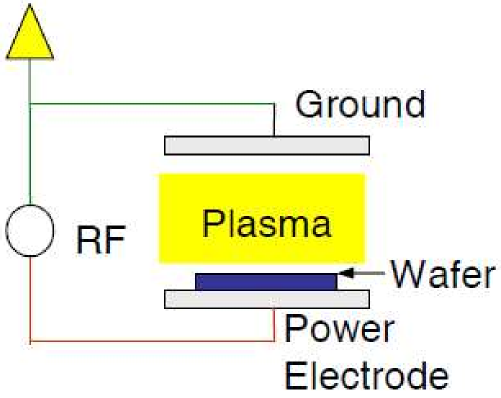
# Modes of plasma etching

## Plasma Etching



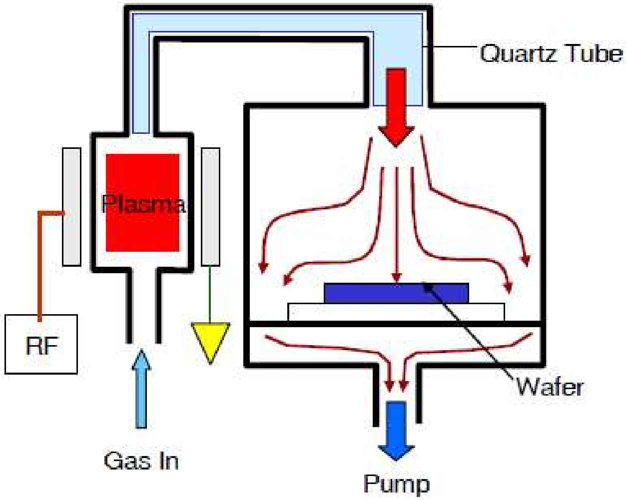
- Substrate on ground electrode
- Less ion bombardment
- Medium etch rate and selectivity

## Reactive Ion Etching



- Substrate on power electrode
- Intense ion bombardment
- High etch rate, Low selectivity

## Remote Etching



- Substrate not in plasma region
- No ion bombardment
- Pure chemical etch
- No radiation damage
- High selectivity
- Isotropic etching

# Main issues in plasma etching

**Profile**
- **Isotropic**
- **Anisotropic**
- Mixed profile

**Undercut**
**Aspect ratio**
**Pattern density**

**Selectivity**
- **Flim/PR or Film/Mask**
- **Film/Underlayer**

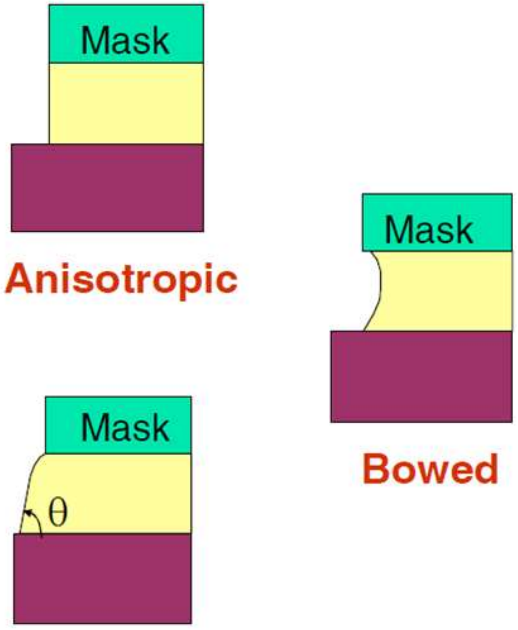
**CD Loss**
**Hard mask**
**Chemistry**

**Uniformity**
- **Across a wafer (Local)**
- **Variations with feature size**
- Wafer to wafer (Global)

**Macro-loading**
**Micro-loading**
**ARDE effect**

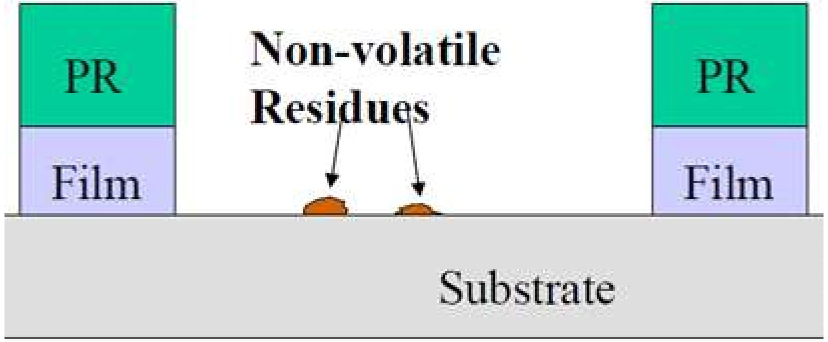
**Surface quality**
- **Contamination**
- **Damage**
- Texture

**Polymer Residue**
**Corrosion**
**Micro-trench & notch**



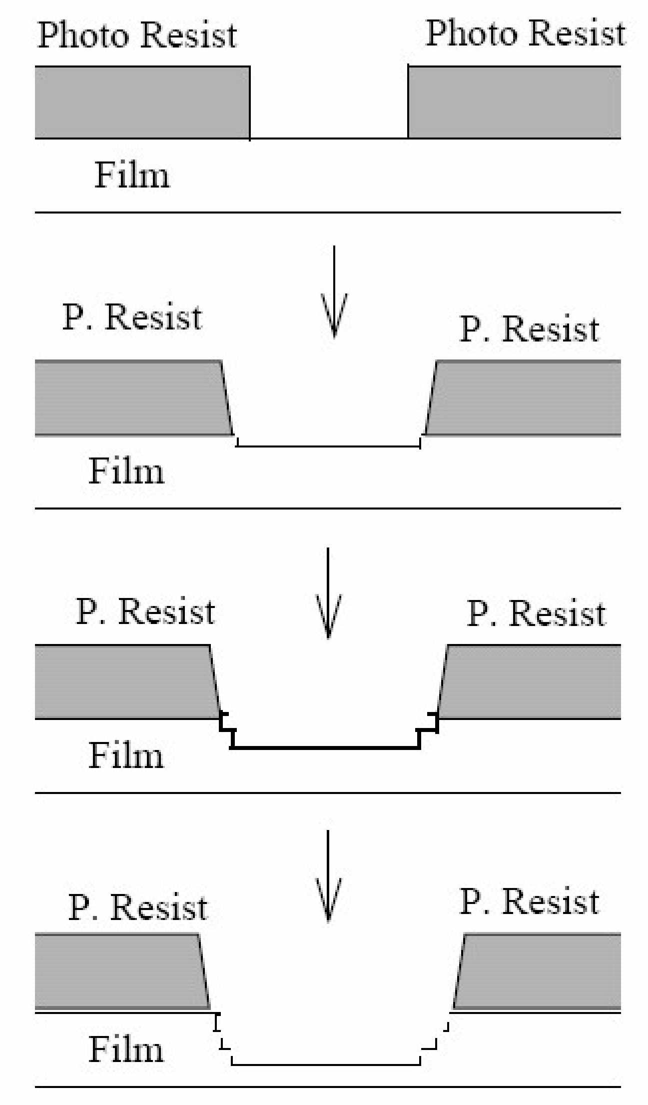
**Anisotropic**
**Bowed**
**Tapered or Sloped**

Etch profiles

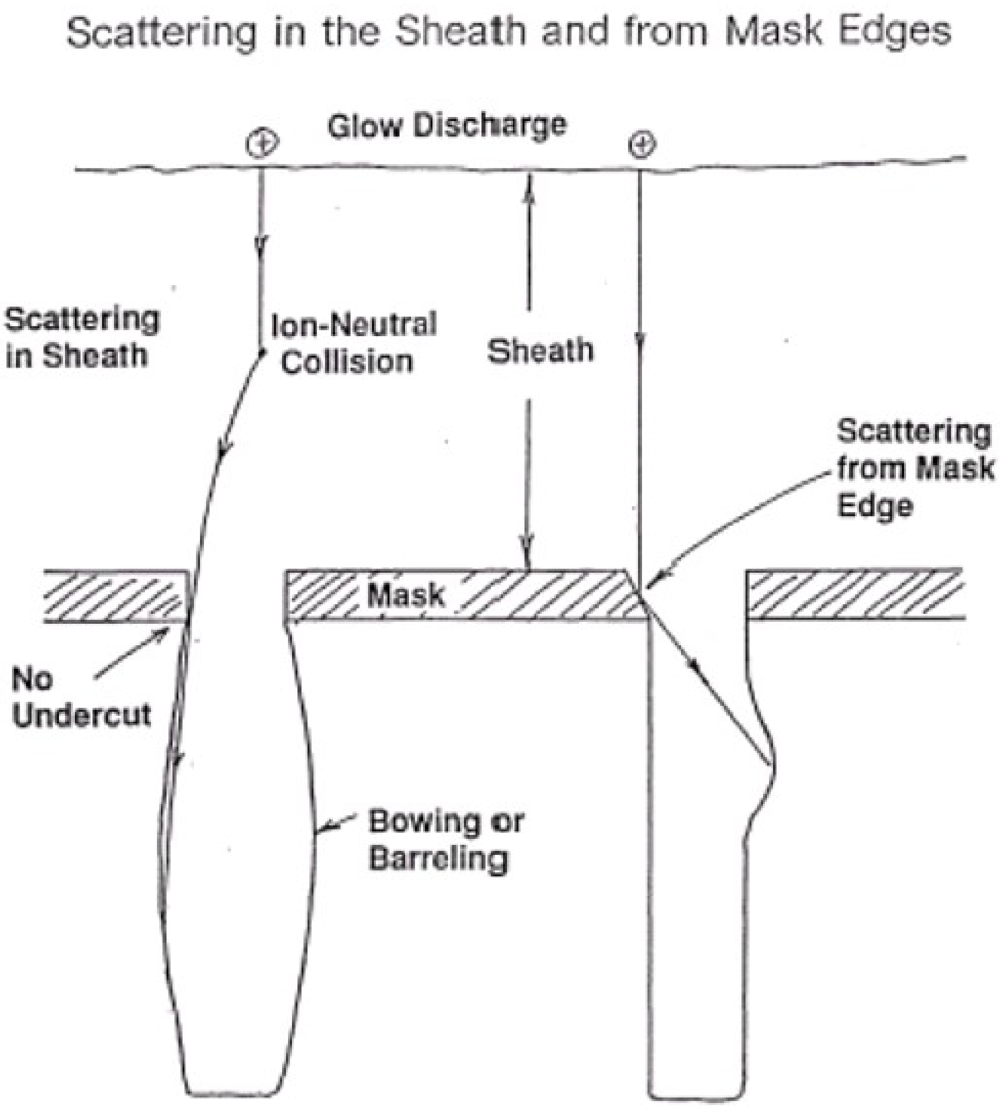


PR: photoresist
CD: critical dimension

# Etched profile control



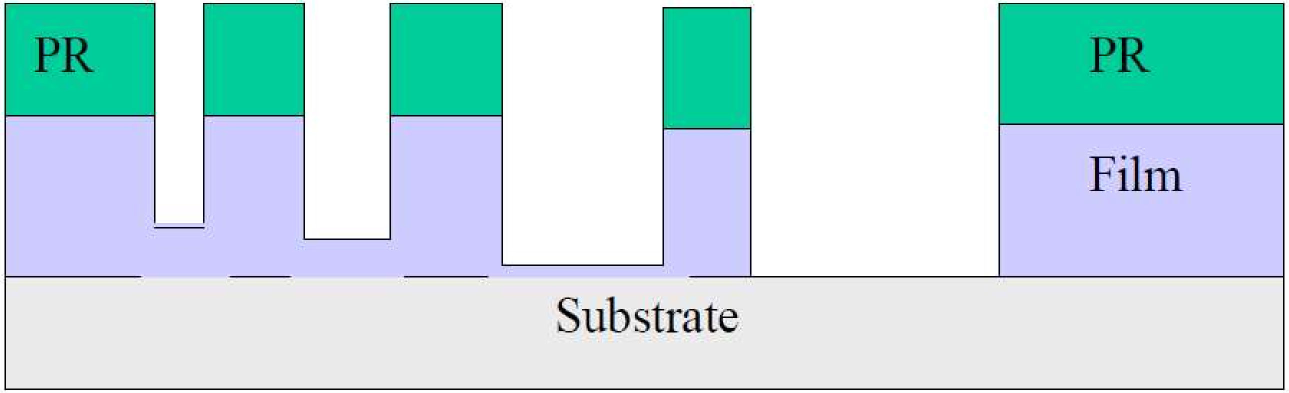
Lateral etch of resist widens the opening gradually.

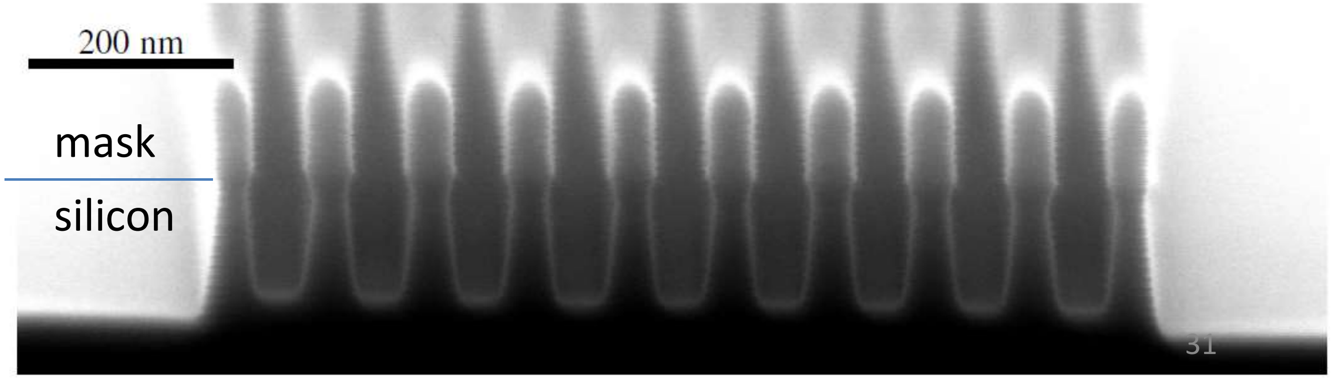


Ion trajectory problem causes bowing profile

# Aspect ratio and micro-loading effect

- Micro-loading: etch rate depends on local pattern density.
- Aspect-ratio dependent etching:
  - Etchants are more difficult to pass through the smaller hole.
  - products are harder to diffuse out.
- Lower pressure can minimize the effect: more directional and longer mean free path, easier for etchants to reach the trench/hole bottom and for etch byproducts to get out.





# Plasma etch methods for various films: overview

- Most reactant gasses contain halogens: F, Cl, Br, or I
- Exact choice of reactant gasses to etch each specific film depends on
    - Ability to form volatile by-products that can be removed by pumping
    - Selectivity and anisotropy.
- Boiling points are good indicators of volatility of species
    - Lower boiling point, higher tendency to evaporate.
    - High boiling point may need etching at elevated temperatures.

# RIE/plasma etch gases: Typical gases for films used in IC fabrication

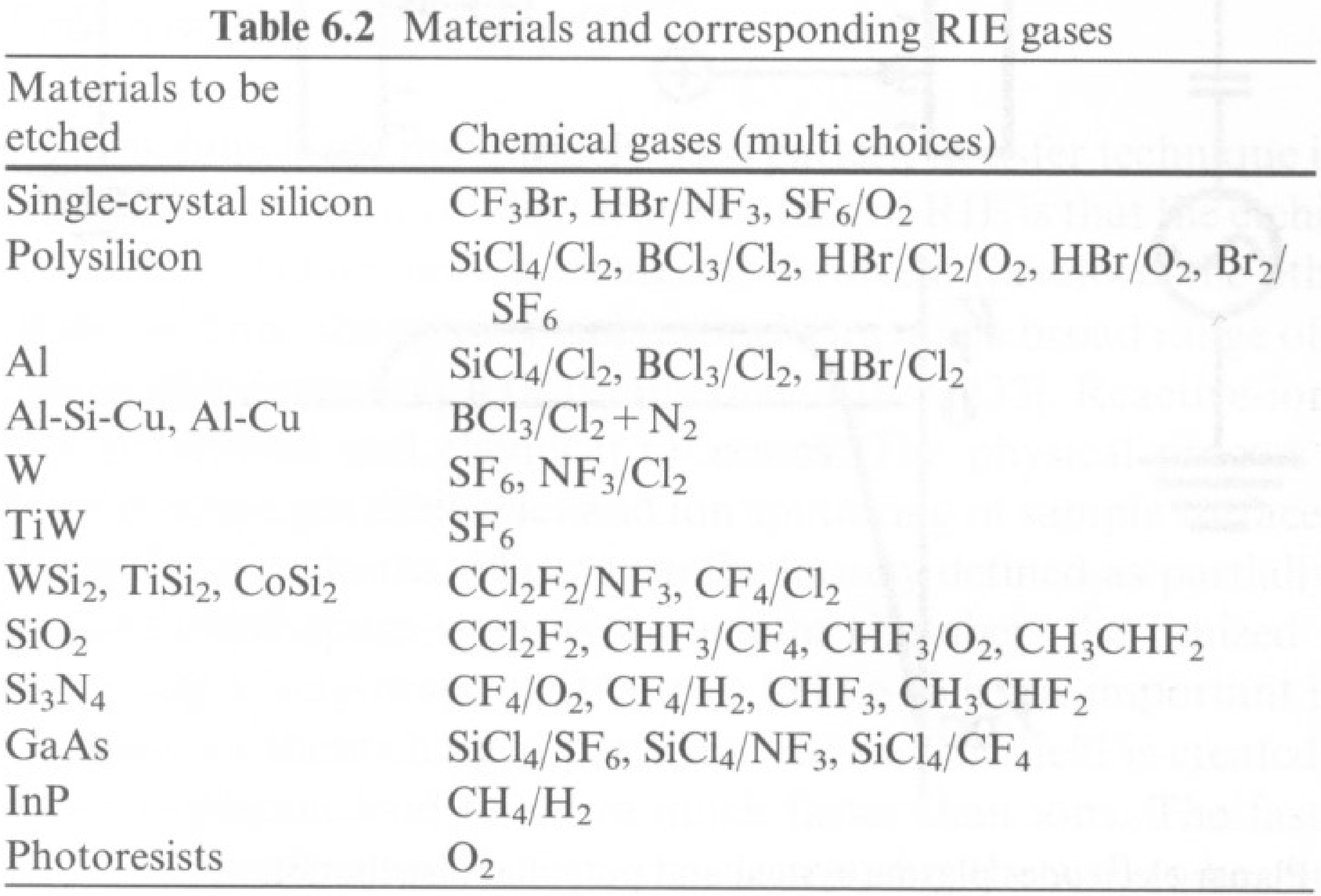


Table 6.2 Materials and corresponding RIE gases

| Materials to be etched | Chemical gases (multi choices) |
|---|---|
| Single-crystal silicon | $CF_3Br$, $HBr/NF_3$, $SF_6/O_2$ |
| Polysilicon | $SiCl_4/Cl_2$, $BCl_3/Cl_2$, $HBr/Cl_2/O_2$, $HBr/O_2$, $Br_2/SF_6$ |
| Al | $SiCl_4/Cl_2$, $BCl_3/Cl_2$, $HBr/Cl_2$ |
| Al-Si-Cu, Al-Cu | $BCl_3/Cl_2+N_2$ |
| W | $SF_6$, $NF_3/Cl_2$ |
| TiW | $SF_6$ |
| $WSi_2$, $TiSi_2$, $CoSi_2$ | $CCl_2F_2/NF_3$, $CF_4/Cl_2$ |
| $SiO_2$ | $CCl_2F_2$, $CHF_3/CF_4$, $CHF_3/O_2$, $CH_3CHF_2$ |
| $Si_3N_4$ | $CF_4/O_2$, $CF_4/H_2$, $CHF_3$, $CH_3CHF_2$ |
| GaAs | $SiCl_4/SF_6$, $SiCl_4/NF_3$, $SiCl_4/CF_4$ |
| InP | $CH_4/H_2$ |
| Photoresists | $O_2$ |

Most lab systems have only fluorine-based gases ($SF_6$, $CF_4$, $CHF_3$) since they are relatively safe; chlorine-based gases are corrosive. Most RIE has Ar and $O_2$ gas, some has $H_2$ and He.